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Outgassing, photoablation and photoionization of organic materials by the electron-impact and photon-impact methods

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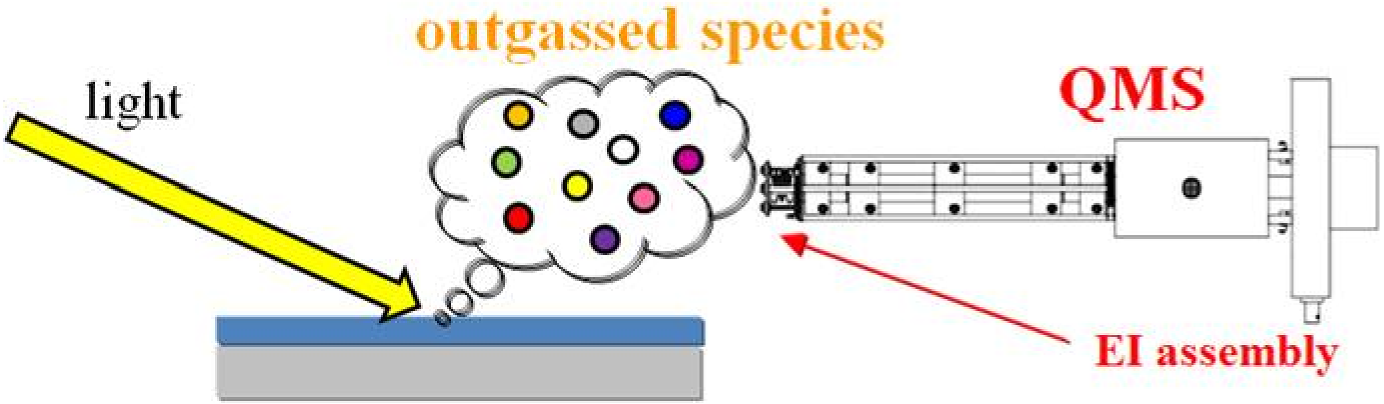
1. Introduction - Measuring "Gases" at NSRRC

- Detection of outgassed species from resist: Typically using a quadrupole mass spectrometer (QMS) under the "residual gas analyzer" (**RGA**) mode (i.e. by the electron-impact ionization (**EI**) method).
- Outgassed species = Dissociated ions and neutrals liberated from the resists into vacuum.

- **How good it is to measure "gases" qualitatively and quantitatively at NSRRC in Taiwan?**

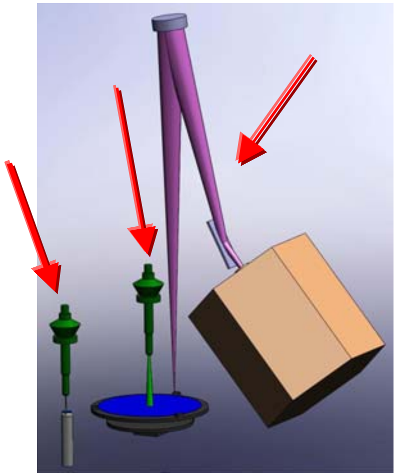
- We measured EI spectra of twelve organic solvents and compared our results with those given by NIST and MSSJ.
- We benchmarked our quantitative outgassing results of counting resist outgassing to those reported by other institutes.
- We conducted outgassing measurement at OOB, EUV, and BEUV wavelengths.



1. Introduction –

Electron- or Photon-impact Source for Resist Testing?

RESIST TESTING TOOLS FOR THE NXE PLATFORM



E-gun

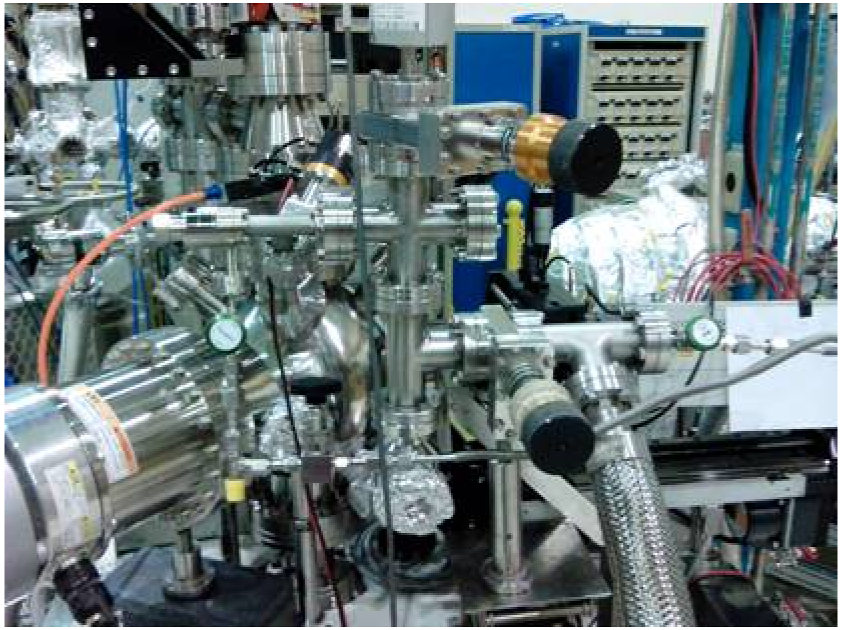
- **Electron energy (100 eV to 5000 eV)**
- **Matching EUV photon exposure ?**

Reported by Rupert C. C. Perera, et al. of **EUV Tech**
http://ieuvi.org/TWG/Resist/2012/093012/6__Pererra_Resist_TWG_2012.pdf

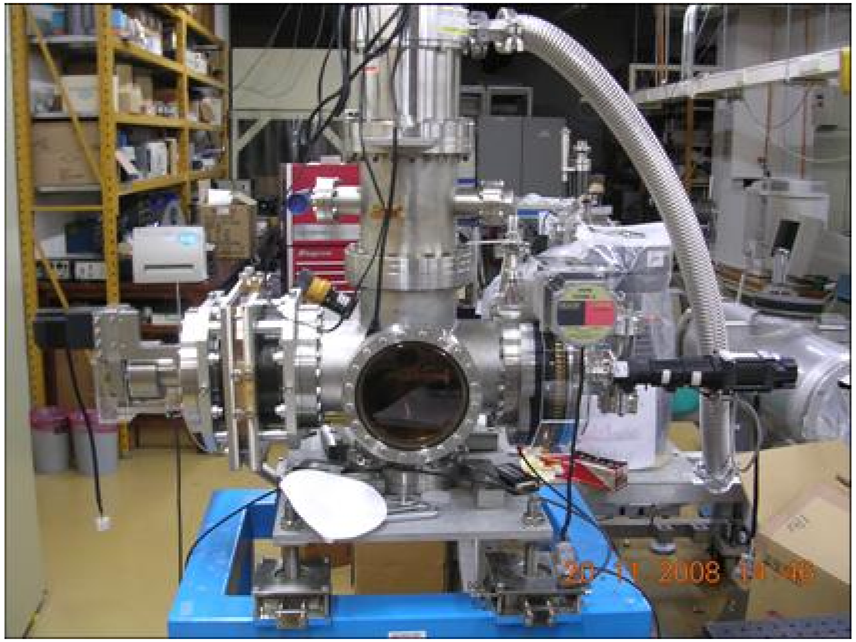
- **Electron vs. photon, do they have similar reaction patterns?**
- **Electron- or photon-stimulated outgassing (RGA/QMS)**
  - We used 12 organic solvents as model samples.
- **Electron- or photon-assist contamination (Witness plate)**
  - We measured EI and PI spectra in the threshold – 200 eV range.

2. Experimental

Quadrupole mass spectrometer

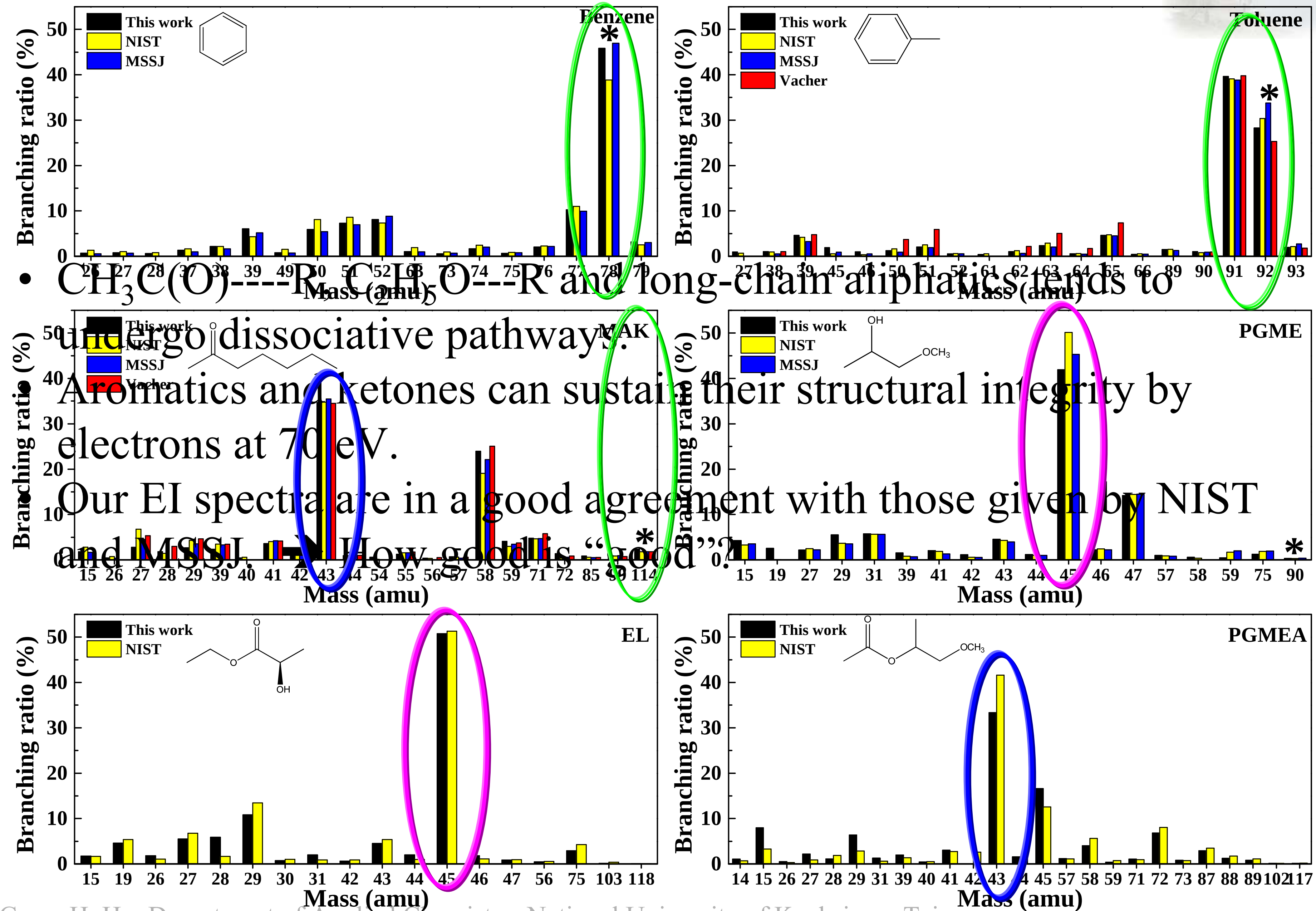


Vacuum compatible specular reflectometer



- **Light source** – **UV(OOB)** from 04B-beamline, **13.5** and **6.7 nm** from 08A-beamline at NSRRC in Taiwan.
- **Resist preparation** at NCKU.
- **Thin-film metrology** – (a) specular ellipsometry at NCKU (b) α -step profilometer at NSYSU.

3.1. The Accountability to Measure "Gases" at NSRRC



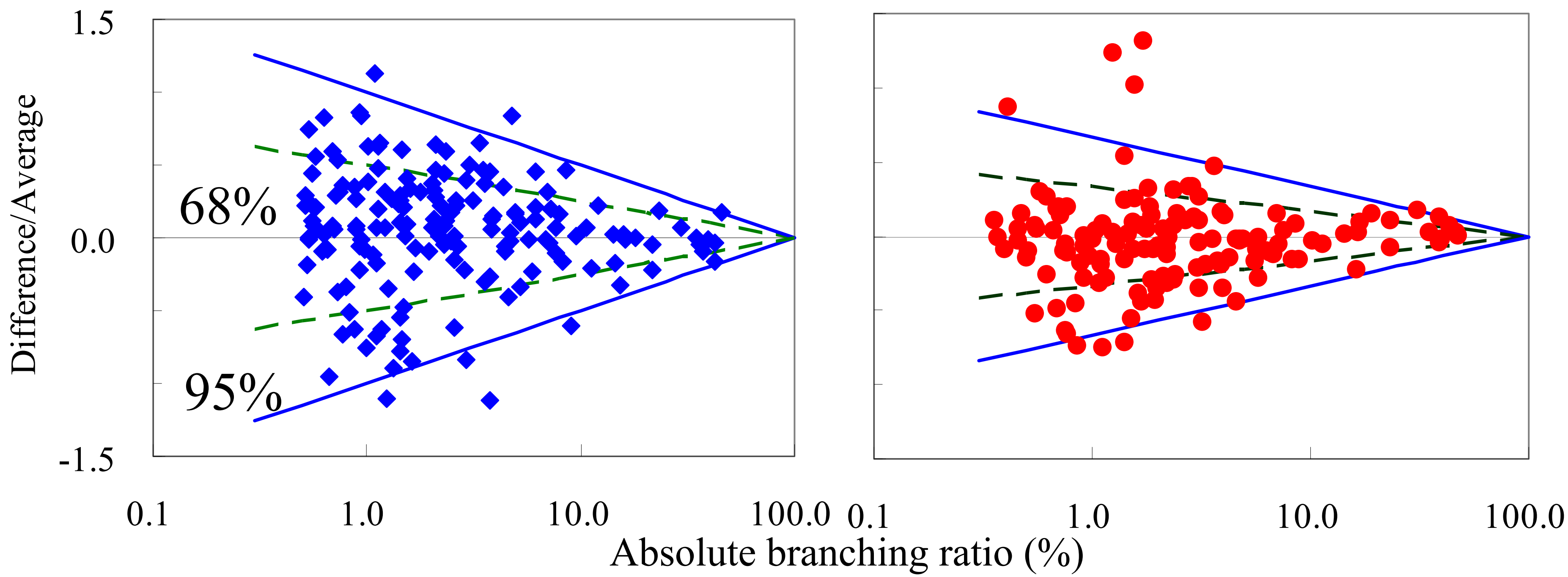
- $CH_3C(O)$----R, C_2H_5O---R and long-chain aliphatics tends to undergo dissociative pathways.
- Aromatics and ketones can sustain their structural integrity by electrons at 70 eV.
- Our EI spectra are in a good agreement with those given by NIST and MSSJ. → How good is "good"?

3.1. The Accountability to Measure "Gases" at NSRRC

• How good it is to measure "gases" **qualitatively** at NSRRC?

- Benchmarking most ion features of the EI spectra to those reported by

NIST Chemistry WebBook **JMMS MassBank**



• Instrument-to-instrument (ItI) uncertainty is mainly statistic; i. e.

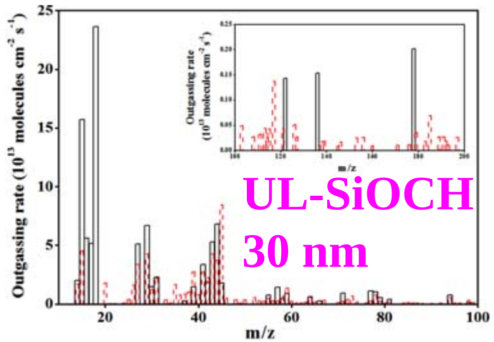
• The ItI uncertainty of this work wrt JMSS (Hitachi series) is ~ 35% better than that wrt NIST (unspecified instruments).

3.1. The Accountability to Measure "Gases" at NSRRC

- How good it is to measure "gases" **quantitatively** at NSRRC?

TABLE I. Absolute outgassing rates of PMMA, RRR, and underlayer films upon irradiation at 13.5 nm.

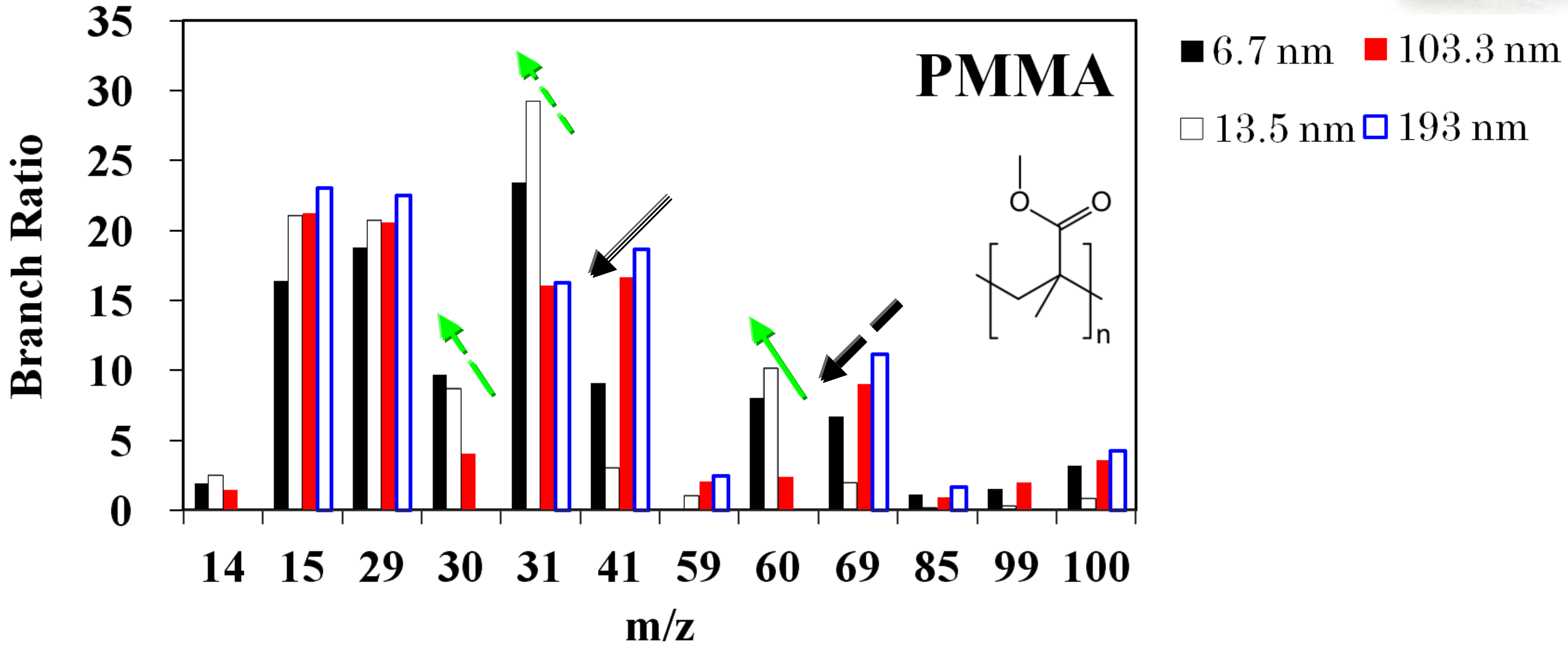
		Outgassing rate, molecules $cm^{-2}s^{-1}$				
		This work				
		Scaled to 15 mW cm^{-2}		Scaled to 10 mW cm^{-2}		
Sample	Thickness (nm)	13–200 m/z[a]	35–200 m/z (excluding 44)	13–200 m/z[a]	45–200 m/z	Previous works
PMMA	125	$(2.2 \pm 0.5) \times 10^{15}$	$(2.1 \pm 0.9) \times 10^{14}$			
	100	2.3×10^{15}	1.4×10^{14}			$(3.3 \pm 0.5) \pm 10^{14}$[b]
	80	2.3×10^{15}	2.5×10^{14}			
RRR	125	8.9×10^{14}	5.4×10^{14}			$(3.2, 7.5) \times 10^{14}$[c]
	100	8.4×10^{14}	5.4×10^{14}			
UL-SiOCH	30			4.3×10^{14}[d]	7.2×10^{13}	4.1×10^{14}[e] 1.4×10^{14}
				6.5×10^{14}		
UL-CHO-1	15	2.2×10^{14}	2.3×10^{13}	1.5×10^{14}	1.6×10^{13}	
UL-CHO-2	15	2.7×10^{12}	2.7×10^{12}	1.8×10^{12}	1.8×10^{12}	



G. H. Ho, et al., JVSTB 30 (2012) 051602

- **Our facility at NSRRC can be one of the limited facilities worldwide capable of measuring resist outgassing in quantity.**

3.2. Resist Outgassing - Wavelength Dependency



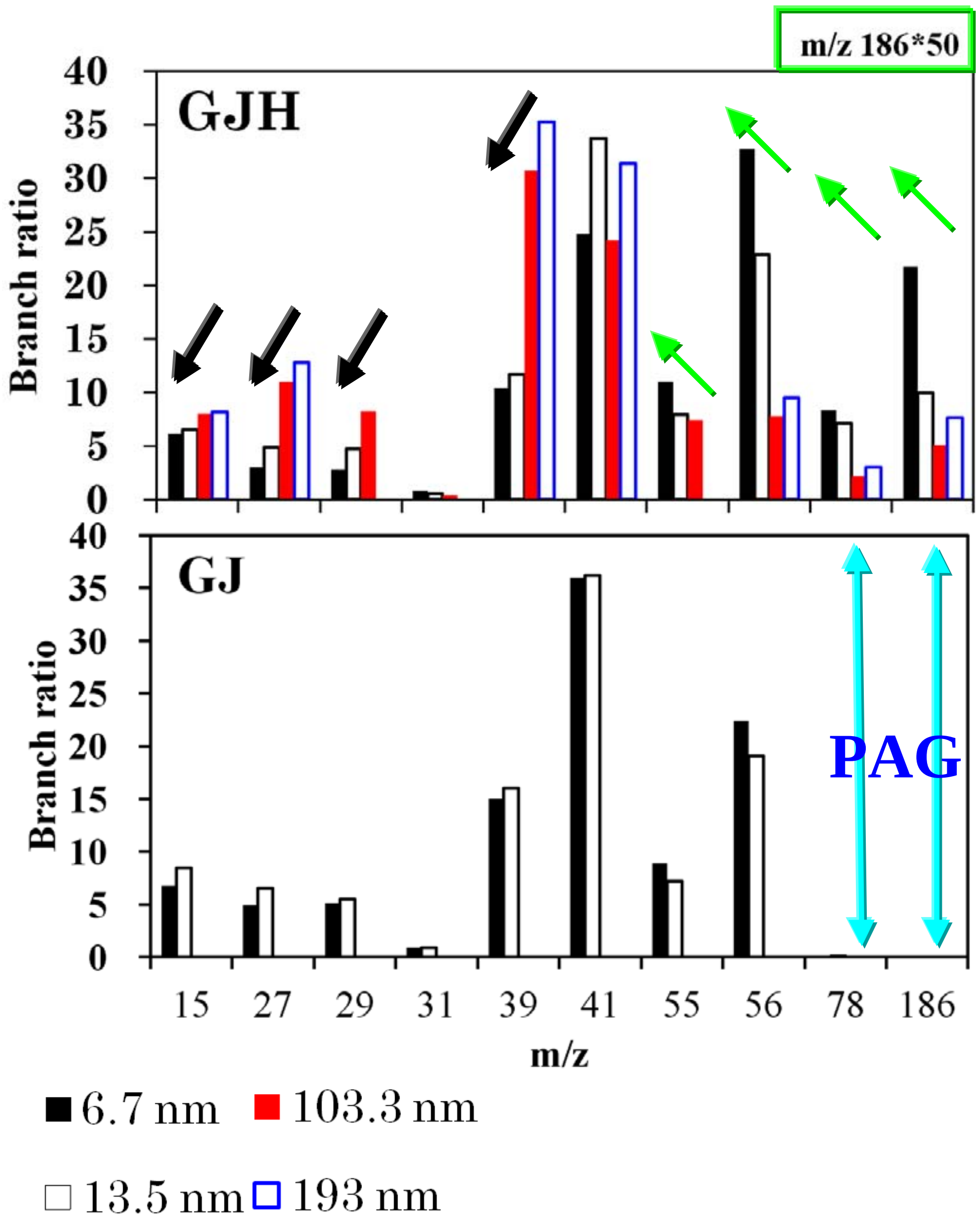
Fragmentation pairs:

$69 - 31(30) = C_4H_{5,4}O - CH_3O$

$59(60) - 41 = HC(O)OCH_3 - C_3H_5$

Wavelength effect on PMMA: Fragmentation partition within the unit of the resin base.

3.2. Resist Outgassing - Wavelength Dependency



Wavelength effect on PS-tBA, GJ:

- Fragmentation partition within the deprotection group (tert-butyl).
- Outgassing from resin backbone is not important.

Wavelength effect on the added 5 wt% PAG ($(C_6H_5)_3SC_4F_9SO_3$), GJH:

- PAG outgassing is in the order of BEUV > EUV > OOB.

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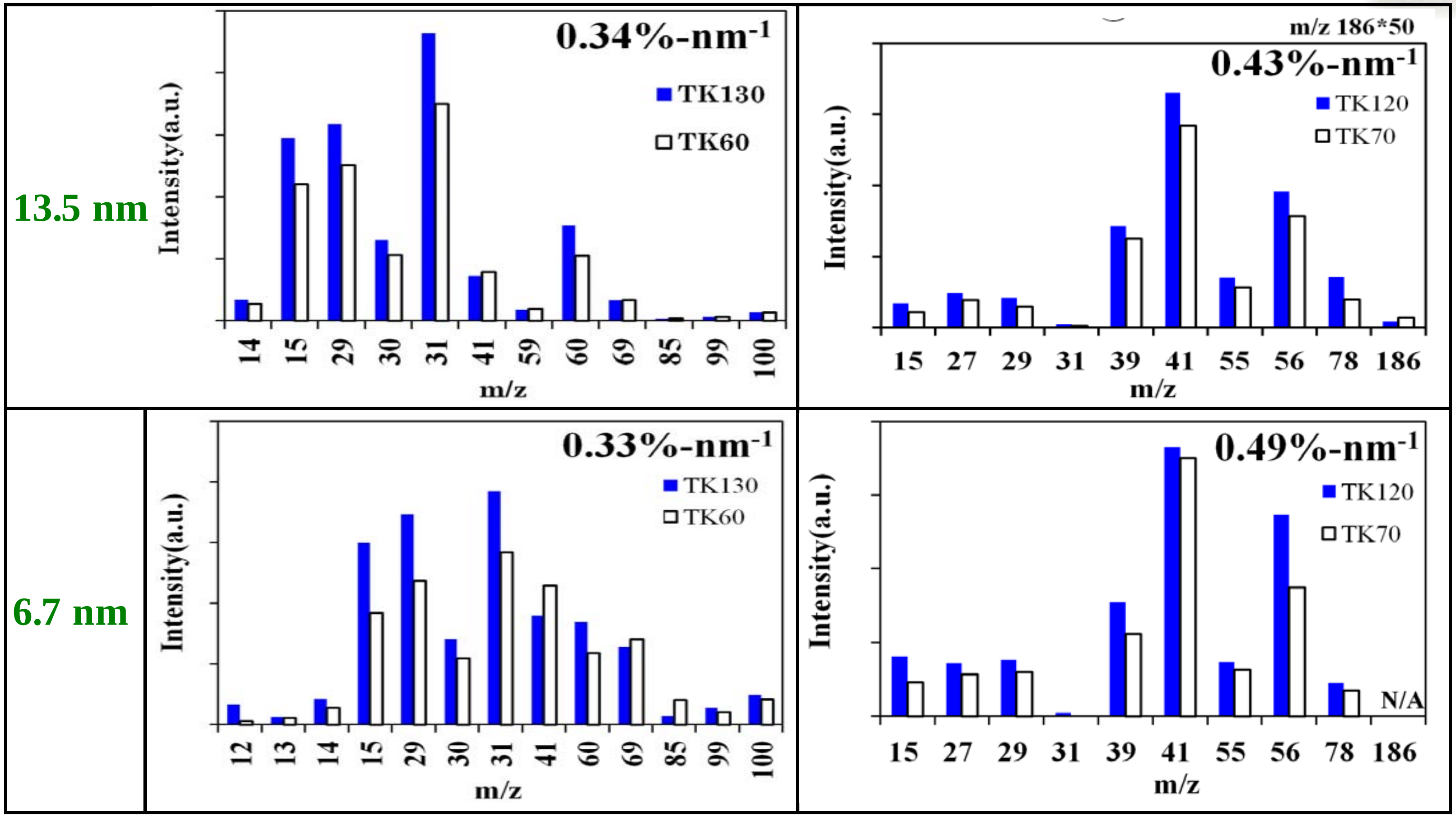
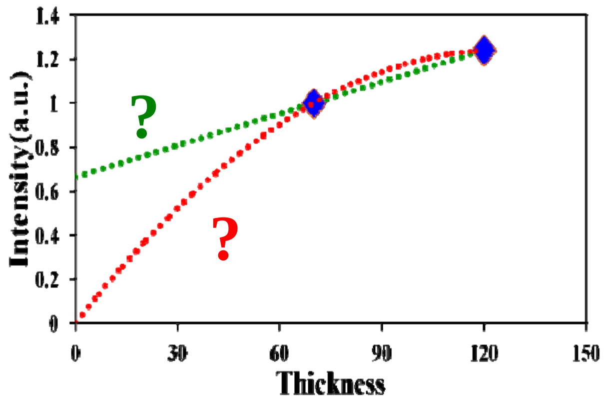
3.2. Resist Outgassing - Thickness Dependency



$$\text{Thickness dependency}\ (\%\text{-nm}^{-1}) = \left(\frac{\Delta\text{Intensity}}{\text{Mean Intensity}}\right) \Big/ \Delta\text{Thickness}$$

3.2. Resist Outgassing - Thickness Dependency

Linear or curvy dependence of resist outgassing on thicknesses?



- Linear dependency is more likely to explain what we have found:

- Outgassing is **structural** and **absorption** dependent.

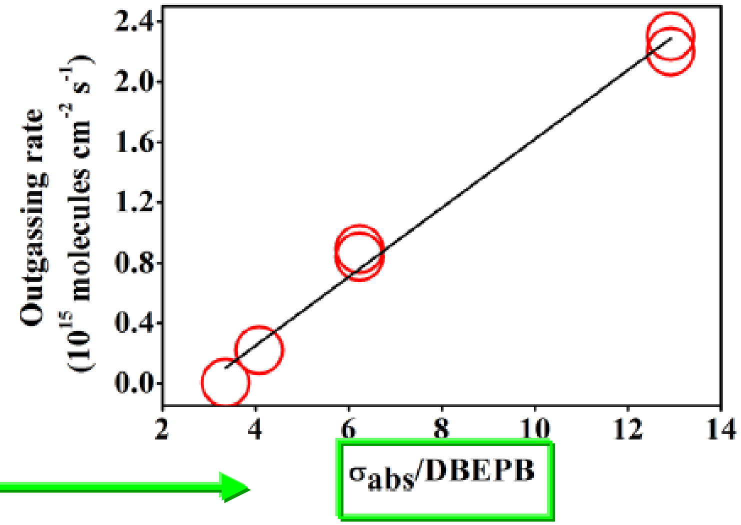


FIG. 8. (Color online) Absolute outgassing rates of PMMA and RRR films of various thickness and 15 nm UL-CHO-1 and UL-CHO-2 films as functions of their respective σ_{abs}/DBEPB values.

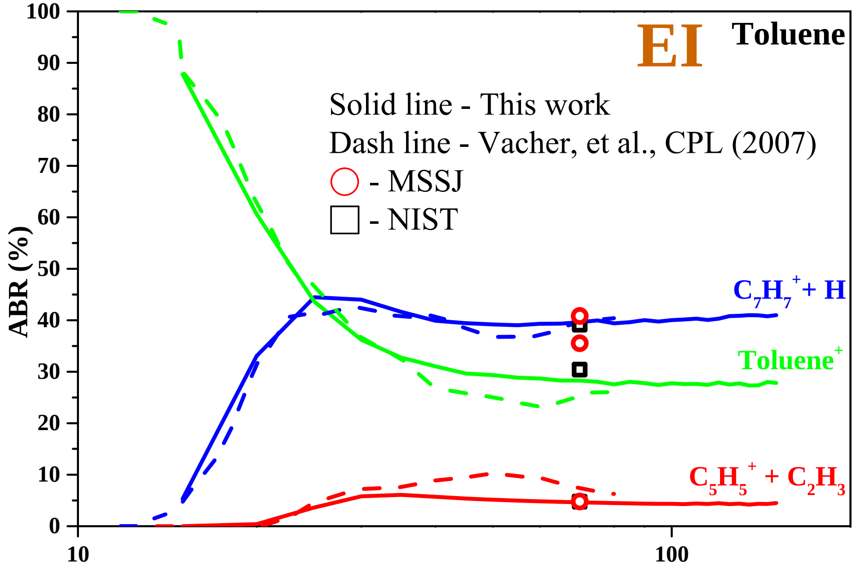
J. Vac. Sci. Technol. B, Vol. 30, No. 5, Sep/Oct 2012

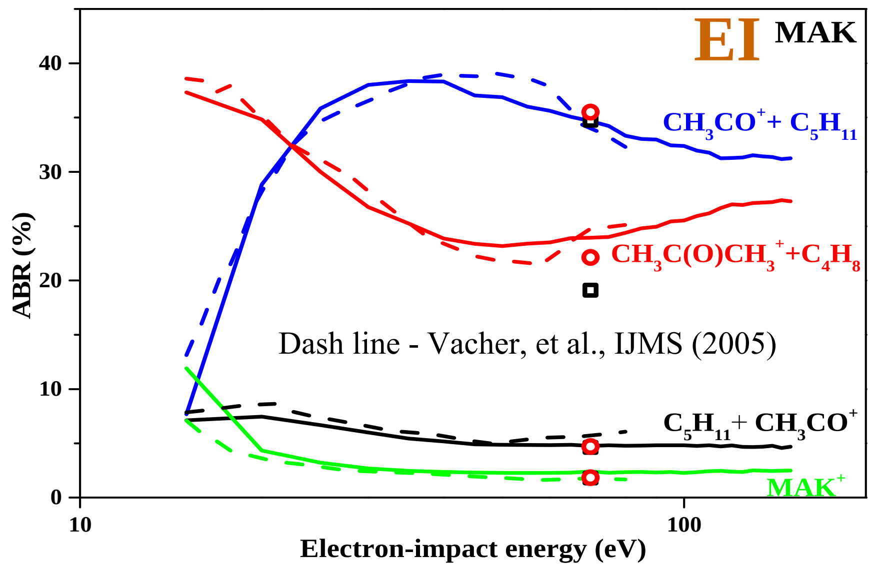
- Thickness effect assessment:
  15 nm and 80 nm films

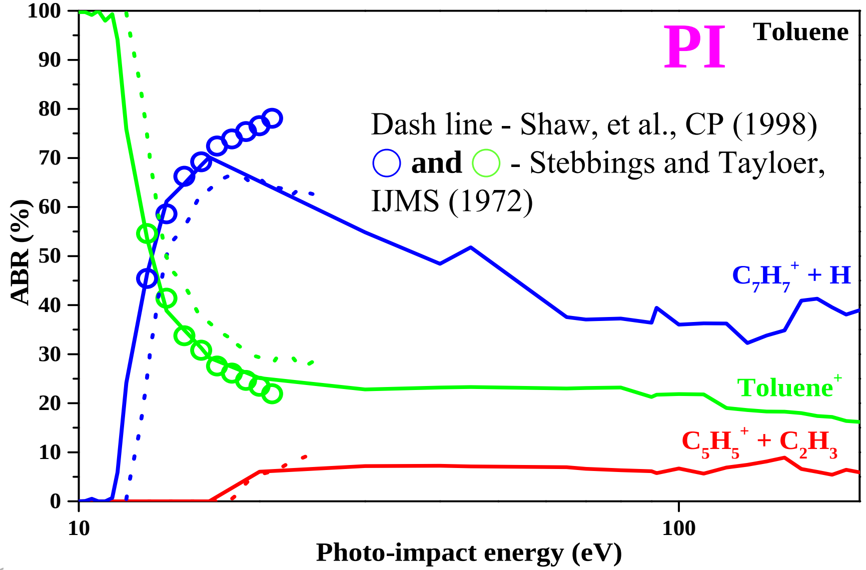
  $0.4\%\text{-nm}^{-1} \times \Delta T \sim 26\%$

3.3. Electron-impact or Photon-impact Source for Resist Testing?

Absolute branching ratio (ABR) of molecular and dissociative ionization over an extensive energy range



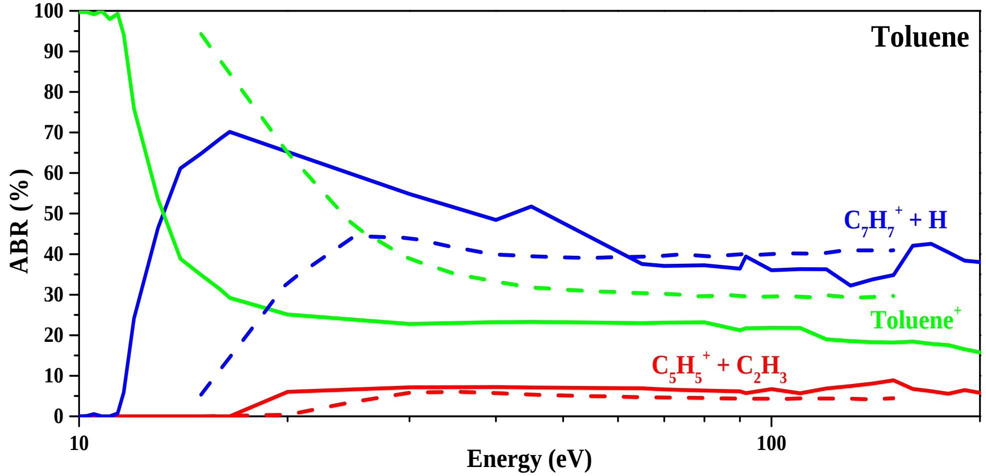




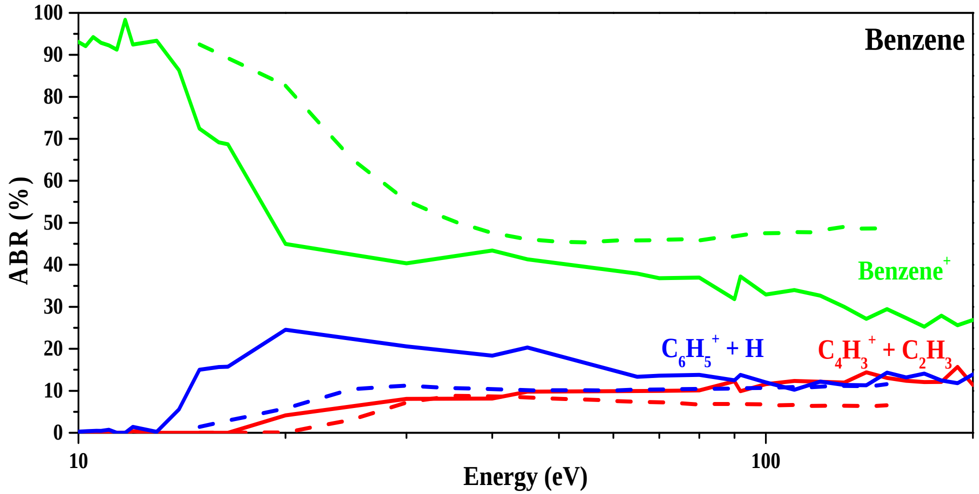
- Very few studies are available for the comparison. **Our results agree with the best available values**.
- The extent of dissociative ionization varies **smoothly and slowly** when the excitation source is above ~50 eV.

3.3. Electron-impact or Photon-impact Source for Resist Testing?

PI vs EI: Aromatics

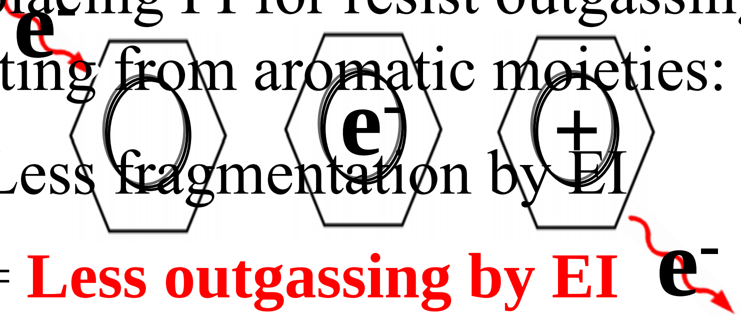


Solid line – PI
Dash line – EI



- **Molecular ions**:
  EI (less fragmentation) > PI
- Benzene has a **negative** electron affinity.

Up to 200 eV assessment about EI replacing PI for resist outgassing testing from aromatic moieties:



- Less fragmentation by EI
  = **Less outgassing by EI**

➔ Under-estimate outgassing with respect to the real case using a photon-impact source?

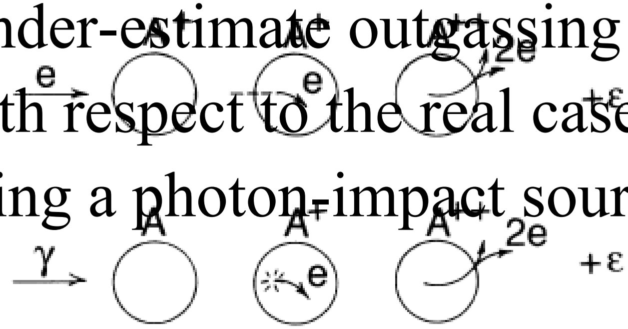


FIG. 1. Comparison for the production of A^{++} by electron-impact ionization of an ion A^+ and by photon-impact ionization of a neutral atom A.

J.A.R. Samson, PRL (1990)

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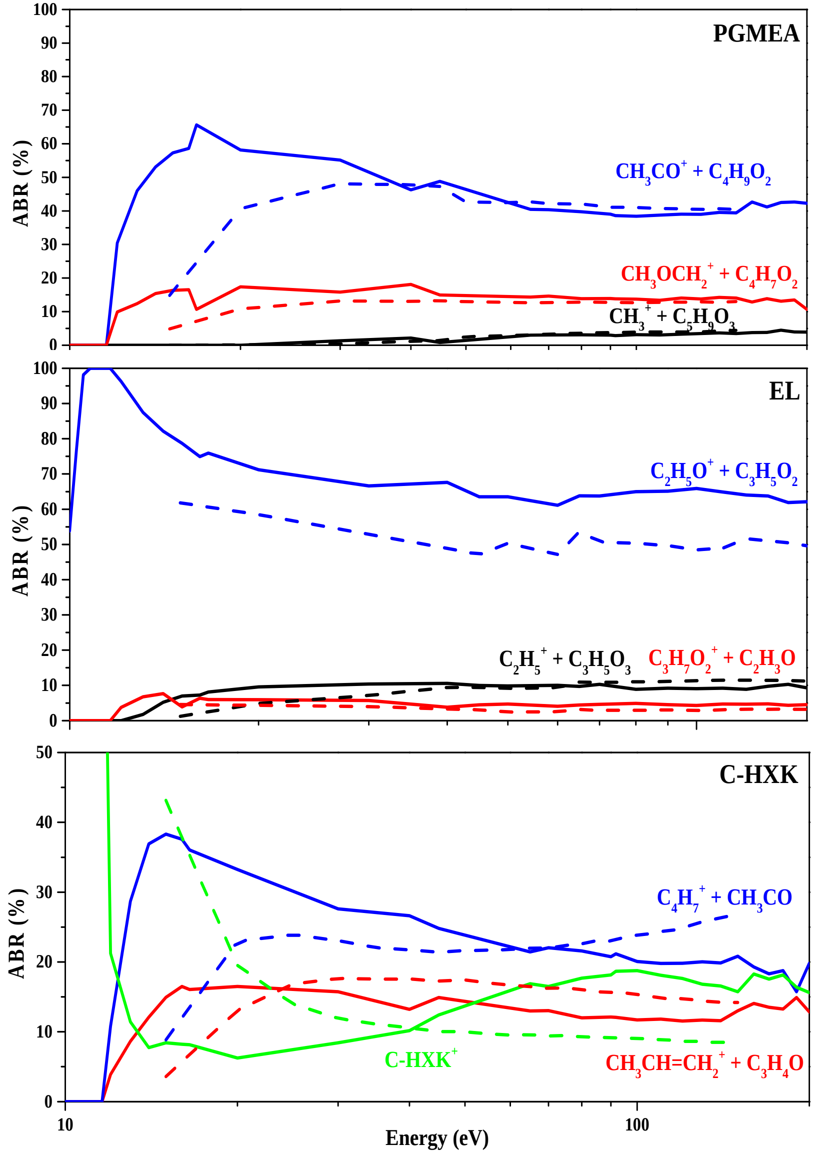
3.3. Electron-impact or Photon-impact Source for Resist Testing?

PI vs EI: few more examples



- **Ketones** can also sustain its molecular integrity but in a less extent than aromatics can.

- **Molecular ions + direct dissociative ionization**: **PI (less fragmentation) > EI**

- **Ketones** (C-HXK, MAK, acetone)
- **Alcohols** and **ether** (Ethanol, CH_3OCH_3)
- **Esters** (PGME, PGMEA, EL, Butylacetate, MMP)

- The fragmentation pattern by EI and PI sources can be alike (PGMEA), different (cyclo-hexanone, C-HXK), or similar (EL).

➔ Not easy to predict what if EI replaces PI for resist testing.

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Summary

- **The accountability to measure "gases"** qualitatively and quantitatively.
- What if the NSRRC site becomes one of the certified site for the outgassing study?

- **Resist outgassing** as functions of wavelengths, film thickness, and resist compositions.
- Fragmentation partition evolved.
- Weak thickness but structural and absorption dependency.

- We have investigated **electron-impact and photon-impact ionization** over an extensive energy range.
- EI vs. PI, alike or dis-alike?

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Acknowledgement

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